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(54) ULTRAHIGH PURITY SILANE AND SILICON PRODUCTION

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ULTRAHIGH PURITY SILANE AND
SILICON PRODUCTION

Abstract of the Disclosure

Tri- and dichlorosilanes formed by the reaction of metallurgical silicon, hydrogen and silicon tetrachloride as subjected to disproportionation in the presence of an ion exchange resin to form high purity silane, with unreacted and by-product materials being recycled. Said chlorosilanes are passed through distillation zones and disproportionation reaction zones to progressively replace chlorine molecules with hydrogen molecules so that product silane is eventually recovered from the process and silicon tetrachloride is recycled for further hydrogenation. The process flow employed ensures that all of the process fluid passes through at least one disproportionation reaction zone for contact with ion exchange resin therein. This ensures that boron impurities present in said fluid are removed to desirably low levels such that ultrahigh purity silane product can be produced. This product can be decomposed in a fluid bed or free space reactor to form ultrahigh purity silicon and by-product hydrogen that can be recycled. The resulting ultrahigh purity silicon can be employed for solar cell and for electronic applications

S P E C I F I C A T I O N

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Background of the Invention

Field of the Invention - The invention relates to the production of ultrahigh purity silane and silicon. More particularly, it relates to an improved process for ensuring the removal of boron impurities to levels required for such production.

Description of the Prior Art - The development of new techniques for the utilization of non-polluting sources of energy is of paramount national and world-wide interest. Solar energy is among the energy sources of greatest interest because of its non-polluting nature and its abundant, non-diminishing availability. One approach to the utilization of solar energy involves the conversion of solar energy into electricity by means of the photovoltaic effect upon the absorption of sunlight by solar cells.

Silicon solar cells, the most commonly employed devices based on the photovoltaic effect, have been employed reliably in space craft applications for many years. For such applications and for industrial and commercial applications in general, crystals of ultrahigh purity, semiconductor grade silicon are commonly employed. Such high purity, high perfection silicon is generally prepared by procedures involving converting metallurgical grade silicon to trichlorosilane, which is then reduced to produce polycrystalline, semiconductor grade silicon from which single crystals can be grown. The costs associated with the production of such high purity, high perfection crystals are high.



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The economic feasibility of utilizing solar cell technology for significant portions of the present and prospective needs for replenishable, non-polluting energy sources would be enhanced if the overall cost of producing single crystal wafers of requisite purity could be reduced. A major area of interest, in this regard, relates to the development of a low-cost, continuous process for the production of high purity polycrystalline silicon from metallurgical grade silicon. The need for such low-cost, high purity silicon is increased by the continued expansion of the utilization of solid-state electronic devices. While the purity requirements for solar grade silicon are not as stringent as for semiconductor or electronic applications, the highest purity silicon material available at economically feasible costs can be effectively utilized for either solar cell or electronic applications.

The initial step of converting metallurgical silicon to trichlorosilane has commonly been carried out by reacting metallurgical grade silicon with HCl in a fluid bed reaction zone at about 300°C. Trichlorosilane comprises about 85% of the resulting reaction mixture, which also contains silicon tetrachloride, dichlorosilane, polysilanes and metal halides. While this technique has been employed successfully in commercial practice, it requires the use of relatively large reaction vessels and the consumption of excess quantities of metallurgical silicon. In addition, the reaction mixture is relatively difficult to handle and has associated waste disposal problems that contribute to the cost of the

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overall operation.

10 In producing high purity polycrystalline silicon from trichlorosilane, current commercial technology is a low volume, batch operation generally referred to as the Siemens process. This technology is carried out in the controlled atmosphere of a quartz bell-jar reactor that contains silicon rods electrically heated to about 1100°C. The chlorosilane, in concentrations of less than 10% in hydrogen, is fed to the reactor under conditions of gas flow rate, composition, silicon rod temperature and bell jar temperature adjusted so as to promote the heterogeneous decomposition of the chlorosilane on the substrate rod surfaces. A general description of the Siemens type process can be found in the Dietze et al patent, US 3,979,490.

20 Polycrystalline semiconductor grade silicon made from metallurgical grade silicon costing about \$0.50/lb. will, as a result of the cost of such processing, presently cost on the order of about \$30/lb. and up. In growing a single crystal from this semiconductor grade material, the ends of the single crystal ingot are cut off, and the ingot is sawed, etched and polished to produce polished wafers for solar cell application, with mechanical breakage and electronic imperfection reducing the amount of useable material obtained. As a result, less than 20% of the original polycrystalline, semiconductor grade silicon will generally be recoverable in the form of useable wafers of single crystal material. The overall cost of such useable material is, accordingly, presently on the order of about \$300/lb. and up. Because of the

relatively large area requirements involved in solar cell applications, such material costs are a significant factor in the overall economics of such applications.

Development efforts to improve high purity silicon technology involve all aspects of the conversion of low-cost metallurgical grade silicon to the presently high cost, high purity silicon product, particularly to means for achieving requisite purity at an economically attractive costs. One aspect of such development work is directed to a process for the production of high purity silane from which silicon can be produced on a continuous basis as hereinafter described. This silane production process involves the hydrogenation of metallurgical grade silicon with hydrogen and silicon tetrachloride to form a gas stream containing trichlorosilane and dichlorosilane. The chlorosilanes are subjected to disproportionation in the presence of an ion exchange resin to progressively replace chlorine molecules with hydrogen molecules so that product high purity silane is eventually recovered from the process and silicon tetrachloride formed during the disproportionation reactions is recycled for further hydrogenation. The process is an integrated one utilizing hydrogen and metallurgical silicon as essentially the only consumed feed materials. The initial tri- and dichlorosilane production step is preferably carried out at elevated pressure and temperature substantially enhancing the conversion rate and the production rate obtainable in a given size reaction vessel. Unreacted silicon tetrachloride is conveniently recycled for reaction with additional quantities of hydrogen and metallurgical silicon. Waste disposal

is readily accomplished, with material wastage minimized, by condensing a minor portion of unreacted silicon tetrachloride from the trichlorosilane reaction mixture, with said condensed silicon tetrachloride and accompanying impurities being passed to waste without the necessity for dilution prior to hydrolysis previously required during waste disposal.

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The high purity silane thus produced can be further purified to remove residual impurities such as trace amounts of monochlorosilane, as required, and may be decomposed on a continuous or semicontinuous basis to produce high purity silicon, e.g. in a fluid reaction zone containing fluidized silicon seed particles or in the hot free space reaction zone of a decomposition reactor. By-product hydrogen produced in the silane decomposition operation can conveniently be recycled to the initial trichlorosilane production step and/or recycled for use as a carrier gas for the silane being decomposed or as a fluidizing gas in the fluid bed silane decomposition operation.

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In such improved processing presently under development, the disproportionation reaction zone actually comprises a separation-disproportionation reaction zone in which progressive conversion of the higher chlorosilanes to lower chlorosilanes and to silane occurs, with staged separation until silane is removed as product and silicon tetrachloride is recycled back to the hydrogenation section. The conversion of the tri- and dichlorosilane feed stream from the hydrogenation reaction is accomplished in a combination of distillation columns and redistribution or disproportionation reaction zones. A process arrangement

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for this purpose was described in the Fourth Quarter, 1977 quarterly Progress Report submitted under the contract referred to above at the beginning of the specification. As described therein, a series of distillation columns is combined with disproportionation reaction zones that process the bottom fraction removed from each distillation column. The high purity silane product is taken from the top of the last distillation column in series, while recycle silicon tetrachloride is taken from the bottom of the first column in series. This process embodiment essentially separates the feedstock into a first trichlorosilane stream, with lighter components as the top draw from the first distillation column, then a dichlorosilane stream, with higher components, as the overhead draw from the second column, then monochlorosilane, and lighter components, as the top draw from the third column, and finally the silane product as the top draw from the last column. The bottom draw from each column is processed through a redistribution or disproportionation reaction zone in order to shift the feed chlorosilane fraction to a range of chlorosilane components as based on chemical equilibrium. This shift or equilibrium redistribution of the chlorosilane feedstock is commonly referred to as disproportionation as this term is used herein. The process stream from each disproportionation reaction zone becomes feedstock for the next preceding distillation column. On an overall basis, this arrangement has the function of processing the initial feedstock comprising primarily trichlorosilane, with minor amounts of lighter chlorosilanes, i.e. dichlorosilane, and silicon tetrachloride such that high purity silane

is ultimately removed as product and silicon tetrachloride is recycled for further hydrogenation. Variations of this basic arrangement include the replacement of the final silane purification distillation column with a combined partial condensation and adsorption purification step. The partial condensation produces a high silane content vapor fraction and a liquid fraction containing primarily the lighter chlorosilanes. The liquid fraction can be processed in a redistribution reactor for recycle, whereas the vapor fraction is further purified in the adsorption step. Such purification step could conveniently operate carbon beds on a thermal swing cycle to produce an ultrahigh purity silane product and a bottoms stream for recycle.

The improved process as described conveniently enables each lower boiling fraction to be separated from the mixture and passed to the following column, with the bottoms of each column being processed through a disproportionation reaction zone for recycle to the previous column.

While such a process arrangement is very workable, it nevertheless requires essentially a paired column and disproportionation reactor for each chlorosilane component. Simplification and reduction of necessary processing equipment is always desired as part of the overall effort to reduce the cost of silicon and enhance the technical and economic feasibility of utilizing low-cost, high purity silicon for practical commercial solar cell and electronic applications.

The improved process arrangement also has a potential

disadvantage related to boron impurities present in the metallurgical grade silicon used as feedstock for the overall process. Boron is an extremely electrically active component that is a very undesirable impurity in the high purity silane and silicon product produced from said metallurgical grade silicon.

10 The boron impurities present in the trichlorosilane-containing gas stream passed from the initial metallurgical silicon hydrogenation step, and not removed in the preliminary silicon tetrachloride condensation step referred to above, can generally be removed upon contact with the ion exchange resin employed in the disproportionation zone. Thus, the boron-containing compounds present in the process fluid form complexes with the resin, thereby trapping the boron impurities and preventing their passage through the process to the silane product. As the above-described process arrangement provides for the treatment of the heavy fractions of the process fluid streams in the disproportionation reaction zones, however, 20 lighter boron components conceivably could pass, with the overhead streams, through the column section, i.e. through the separation-disproportionation section, into the high purity silane and silicon product. As it is needed for some silicon applications to achieve boron impurity levels of less than one part per billion, it will be appreciated that such passage of small amounts of boron impurities into the product silicon removed from the final distillation separation zone is a matter of significant concern in high purity silane and silicon production operations. While the silane may be treated in an additional zone

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10 prior to being decomposed to form high purity silicon, the use of beds of activated carbon, silica gel or other commercially available adsorbents suitable for removing trace quantities of monochlorosilane, are not generally effective for removing boron impurities from the silane gas stream. Other purification techniques can be employed for such purpose, and may be employed as a redundancy feature in any event to assure ultrahigh purity. It is desirable, however, that the basic process arrangement prevent, to the fullest extent possible, boron impurities from passing through to the silane product as well as providing the reduced processing and equipment costs needed to facilitate the product of low-cost, ultrahigh purity silane and silicon for practical commercial operations.

It is an object of the invention, therefore, to provide an improved process for the production of ultrahigh purity silane and silicon.

20 It is another object of the invention to provide an improved process for the low-cost conversion of metallurgical grade silicon to ultrahigh purity silane and silicon.

It is another object of the invention to provide an improved integrated process for the production of low-cost, high purity silane and silicon, advantageously of ultrahigh purity.

It is a further object of the invention to provide a process for the production of silane and silicon ensuring that boron impurities can be effectively limited to ultrahigh purity levels.

Is is a further object of the invention to provide an improved process for the disproportionation of a

chlorosilane-containing process fluid.

It is a further object of the invention to provide a process for the disproportionation of chlorosilanes capable of ensuring the effective removal of boron impurities to ultrahigh purity levels.

With these and other objects in mind, the invention is hereinafter disclosed in detail, the novel features thereof being particularly pointed out in the appended claims.

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Summary of the Invention

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The objects of the invention are accomplished by passing a chlorosilane-containing process fluid stream comprising tri- and dichlorosilane to a distillation zone for separation into an overhead dichlorosilane-rich stream and a bottom trichlorosilane-rich stream both of which are passed to disproportionation reaction zones. The ion exchange resins employed in said zones are capable of effectively removing boron-containing compounds from the process streams passing through said zones. By thus ensuring that all of the process fluid stream actually passes through at least one said reaction zone for contact with ion exchange resin therein, it is thereby ensured that the boron impurities that may be present in the process fluid stream can be removed to the desirably low level required for ultrahigh purity silane product. In the integrated process for producing high purity silane and silicon from metallurgical grade silicon, the tri-chlorosilane-containing gas stream obtained by hydrogenation of metallurgical silicon with hydrogen and silicon tetrachloride can be passed to a preliminary distillation

10 zone for separation of unreacted silicon tetrachloride from the process fluid stream containing said trichlorosilane and dichlorosilane, which are separated as indicated above. The disproportionation reactions are utilized in combination with appropriate distillation separation operations such that high purity silane is recovered as overhead from the last column and additional recycle silicon tetrachloride is removed from the bottom of said preliminary separation zone. Trace amounts of monochlorosilane can be removed from the product silane in a separate purification zone, with the ultrahigh purity silane of desirably low boron impurity levels being suitable for use in the production of low-cost, ultrahigh purity silicon on a continuous or semicontinuous basis in the hot free space zone of a decomposition reactor or in a fluid bed reaction zone. By-product hydrogen can be recycled to the metallurgical silicon hydrogenation step or can be employed as a carrier gas in said silane decomposition reaction.

Brief Description of the Drawings

20 The invention is further described with reference to the accompanying drawings in which:

Figure 1 illustrates a known process for the production of high purity silane by the disproportionation of chlorosilanes; and

Figure 2 illustrates the process flow employment in the practice of the present invention for ensuring the capability of removing boron impurities to the levels required for the production of ultrahigh purity silane and silicon.

Detailed Description of the Invention

The process of the invention is herein described and claimed with reference to an integrated process capable of producing ultrahigh purity silane or silicon from metallurgical grade silicon. The invention ensures the capability of achieving the low boron impurity levels required for the production of ultrahigh purity material. The overall process includes (1) the production of trichlorosilane from metallurgical silicon and hydrogen, (2) the disproportionation of the trichlorosilane containing gas stream to produce high purity silane, and (3) the conversion of said silane to high purity silicon, if desired. The integrated process effectively recycles unreacted and by-product materials, minimizing material wastage and simplifying waste disposal operations. The present invention ensures the effective removal of boron impurities from said trichlorosilane-containing stream or from any other chlorosilane-containing gas stream subjected to said disproportionation to produce silane.

The present invention can advantageously be employed in the conversion of the conventional metallurgical grade silicon materials available in the art to desired high ultrahigh purity silane or silicon. Metallurgical grade silicon, as referred to herein, is a grade of silicon having a resistivity generally on the order of about 0.005 ohm-cm and up to about 3% iron, 0.75% aluminum, 0.5% calcium and other impurities normally found in silicon produced by the carbothermic reduction of silica. It is also within the scope of the invention to employ a ferro-silicon material containing at least about

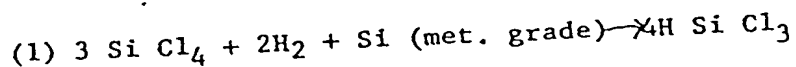
90% Si and up to 10% or more of iron. It will also be understood by those skilled in the art that suitable grades of ferro-silicon material are included within the meaning of the term "metallurgical silicon", as used herein. It will also be understood that particular grades of metallurgical silicon containing unusual concentrations of certain specific impurities, perhaps for example 1% or more of lead, may not be suitable feed material for the process.

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Metallurgical grade silicon or ferrosilicon is processed, in accordance with preferred integrated process, to produce an initial reaction mixture of di- and tri-chlorosilane by a technique that enables the overall process to be carried out in an economically advantageous manner, with the desirable by-product recycle and simplified waste disposal referred to herein. As silicon tetrachloride separated from the reaction mixture can readily be recycled for reaction with additional quantities of metallurgical silicon and hydrogen, high purity silane is produced with said metallurgical silicon and hydrogen being essentially the only major consumed feed materials.

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In this process, metallurgical silicon is initially reacted with hydrogen and silicon tetrachloride in a reaction zone maintained at a temperature of from about 400°C to about 600°C and at a pressure preferably in excess of about 100 psi to form trichlorosilane as follows:



with the reaction (1) mixture containing a yield of about

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20-30% by weight trichlorosilane on a hydrogen-free basis, and of about 0.5% dichlorosilane with the remainder being silicon tetrachloride together with impurities comprising mainly carryover metallurgical silicon powder, metal halides and other impurities essentially without undesired polysilanes.

10 Elevated pressures and temperatures in the reaction zone substantially enhance the production rate obtainable in a given sized reaction vessel and the feed conversion rate, thereby reducing the size requirements for reaction vessels and facilitating the overall production operation. The integrated process for the production of high purity silane and high purity silicon, with simplified feed material and reduced material disposal requirements, is of significant advantage in the production of the desired material at an economically feasible cost for practical commercial operations.

20 The trichlorosilane-containing reaction mixture leaving the reactor zone is desirably cooled to condense a minor portion of the unreacted silicon tetrachloride therein, with said carryover metallurgical silicon, metal halides and other impurities present in said trichlorosilane gas stream separating therefrom the condensed silicon tetrachloride. For this purpose, the trichlorosilane gas stream is passed to a settling zone from which the gas stream passes upward to a condenser unit from which the partially condensed stream is removed. A minor portion of the unreacted silicon tetrachloride, for example on the order of about 5% by weight of the overall silicon tetrachloride in said trichlorosilane gas stream,

10 together with accompanying carryover silicon powder and other impurities is returned to the settling zone from which a waste stream is removed for convenient disposal as the only significant waste stream of the overall integrated process of the invention. Hydrogen gas withdrawn from the condenser unit is recycled for passage with fresh hydrogen to the reactor zone for reaction therein with additional quantities of fresh metallurgical silicon. The trichlorosilane containing gas stream, purified of said impurities and containing said dichlorosilane and the remainder of said silicon tetrachloride, may be subjected to disproportionation by the known process referred to above or, advantageously, by the process of the present invention.

20 In the known process as shown in Figure 1, the indicated trichlorosilane-containing gas stream identified by the numeral 1 is converted and separated into a high purity silane product stream 2 and a silicon tetrachloride stream 3 that can be recycled for reaction with additional quantities of metallurgical silicon and hydrogen. The trichlorosilane-containing gas stream first passes to distillation separation column 4 from which a tri- and dichlorosilane-containing gas stream is separated as overhead from unreacted silicon tetrachloride. The separation is driven by the combination of heat addition at the bottom of column 4 by reboiler 6 and heat extraction by reflux condenser 5 at the top of the column. The overhead stream passes in line 22 to a second column 7 that is operated so that said dichlorosilane and any lighter components present are removed in overhead stream 23, while trichlorosilanes and heaviers are removed from

the bottom of column 7, which is driven by reboiler 9 and reflux condenser 8 and with appropriate heat addition at the bottom and cooling at the top of the column. The bottoms draw of column 7 is processed through disproportionation reaction zone 16 containing ion exchange resin that catalyzes the disproportionation or redistribution of the trichlorosilane in stream 25 to form a spectrum of chlorosilanes including dichlorosilane and silicon tetrachloride together with remaining trichlorosilane as determined by equilibrium considerations. The disproportionation reaction mixture leaving reaction zone 16 passes through line 19 for reintroduction into column 4 as a feed for the initial separation between trichlorosilane and lighter materials from silicon tetrachloride to be recycled.

Overhead stream 23 from column 7 passes to column 10, the third column in the processing arrangement, wherein monochlorosilane is removed as overhead stream 24 and dichlorosilane and heavier materials are removed as the bottoms draw 26. Column 10 is similarly driven by reboiler 12 and reflux condenser 11. The dichlorosilane-containing bottom stream in line 26 passes to disproportionation reaction zone 17 in which dichlorosilane is redistributed to monochlorosilane and trichlorosilane according to equilibrium considerations. The reaction mixture from zone 17 is fed to previous column 7 through line 20.

Overhead stream 24 from column 10 passes to the final column in the processing arrangement, namely column 13. This column is used to separate product silane as overhead in line 2 from any remaining heavier components that are

removed from column 13 as bottom stream 27. Column 13 employs reboiler 15 and reflux condenser 14, with said overhead product silane stream 2 constituting a portion of the stream from the top reflux condenser 14. The heavy bottom stream 27 is passed to third disproportionation reaction zone 18 in which monochlorosilane is redistributed to silane and dichlorosilane. The reaction mixture from said reaction zone 18 passes to the next preceding column 10 through line 21.

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The known process thus provides for disproportionation of the bottoms streams removed from the last three distillation separation columns, with said bottoms streams contacting ion exchange resin in each of the three separate disproportionation reaction zones. As a result of this processing arrangement, lighter materials are progressively increased in concentration in the overhead product, and heavier materials are thus increased in concentration in the bottoms. High purity silane is thus recovered as the final overhead product 2 and silicon tetrachloride is recycled in line 3 for use in the hydrogenation of additional quantities of metallurgical grade silicon in the overall integrated process for producing silane from said metallurgical silicon. As noted above, various process modifications can be employed in said known process, as by replacing the final silane purification column with appropriate adsorption beds to yield a high purity silane product that can be passed to a silane decomposition zone for the formation of a high purity silicon product useful for solar cell and other silicon applications. Impurities desorbed from such adsorption beds, as for example by a

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suitable thermal swing adsorption cycle, can be recycled back to the third column. Since the separation occurring in the third column is between relatively light components with a wide range of boiling points, it is possible to substitute a partial condenser for said third column so that progressive cooling of the silane-rich stream would condense substantial amounts of the dichlorosilane and almost all of the monochlorosilane, so as to leave silane primarily as the feed to the adsorption beds. The condensed fraction can then be recycled for treatment in an appropriate disproportionation reaction zone.

The known process and such variations thereof all involve the progressive separation of higher components as overhead and the successive treatment of the heavier fractions in disproportionation reaction zones. High purity silane is conveniently and effectively produced thereby. In its basic form, the process has the disadvantage of utilizing considerable equipment, with essentially a separation column or zone and a disproportionation reaction zone employed for each separate level of chlorosilane component. In addition, the basic process and its variations all share an important drawback that precludes assurance of boron purity removal to the levels required for ultrahigh purity silane and silicon. As discussed above, such ultrahigh purity is required for electronic applications in which very stringent limitations on the boron impurity level of the silicon pertain and is desirable in silicon for solar cell applications if compatible with the cost restraints applicable for practical commercial solar cell applications. While the

10 preferred ion exchange resins employed in the disproportionation reaction zones readily adsorb and react with boron compounds, and thus serve to trap boron impurities in the chlorosilane-containing process fluid being treated, light boron impurity components, such as diborane (B_2H_6), conceivably might bypass the disproportionation reaction zones and eventually end up with the silane product removed from the process. As only the heavy fractions of the process fluid subjected to the separation-disproportionation reaction are passed directly to the disproportionation reaction zones, the lighter fractions could conceivably pass from one separation column or zone to the next without passage through at least one of such reaction zones. In the absence of subsequent processing to remove such boron impurities that might thus conceivably avoid being trapped by contact with ion exchange resin, the resulting high purity silane may not have boron impurities removed to the very low levels required for ultrahigh purity material.

20 In this regard, it should be noted that final column 13 has, as its primary function, the ensuring of an ultrahigh purity silane product. For this purpose, the column can be operated so that the light component removed as overhead would be silane, having a boiling point of $-112^\circ C$, and said diborane, the lowest boiling electronically active impurity, having a boiling point of $-86^\circ C$, would be recovered as the bottoms stream from the column, which would be operated as a cryogenic distillation zone in which the high purity silane is distilled under pressure. Since boron is such a detrimental impurity and since such stringent purity requirements pertain to ultrahigh

10 B purity applications, it is prudent and indeed imperative to utilize redundant process features to ensure the effective removal of boron impurities to the very low levels required for the production of ultrahigh purity silane and silicon. While portions of the process fluid treated in the distillation and reaction zones of the known process pass through said reaction zones and ^{contact} ~~conduct~~ the ion exchange resin therein, it is not ensured that all of the process fluid thus contacts said resin. As a result, the highly desirable redundancy in the boron removal capability to achieve the less than one part per billion impurity level required for electronic and other ultrahigh purity applications is not achieved.

20 The deficiencies of the known process in this regard are simply and conveniently overcome by the novel and advantageous features of the present invention as illustrated in Fig. 2 of the drawings. As shown therein, the process arrangement includes three distillation separation columns, with associated reboilers and condensers, and two disproportionation reaction zones. A chlorosilane-containing feed stream 50, equivalent to stream 1 of Fig. 1, passes to first distillation column of zone 60, having reboiler 62 and reflux condenser 61, in which tri- and dichlorosilane are separated as overhead in line 53 from unreacted silicon tetrachloride in line 52 that can be recycled to the hydrogenation of metallurgical silicon stage in the overall integrated process to which the invention can be applied. The overhead stream in line 53 is fed to distillation separation column or zone 70, having associated reboiler 73 and reflux condenser 71. Column 70 is operated to

10 separate said stream so as to form a trichlorosilane rich bottom liquid stream. The overhead draw stream in line 58, containing said dichlorosilane and lighter constituents, is passed to disproportionation reaction zone 100, containing suitable ion exchange resin. Said chlorosilanes are redistributed in zone 100 to form a mixture of silane and chlorosilane components. Similarly, bottom draw 57 from said column 70, containing trichlorosilane and heavier components, passes to a second disproportionation reaction zone 90, containing suitable ion exchange resin. Said chlorosilanes are redistributed in zone 90 to form a mixture of chlorosilanes and silicon tetrachloride. Thus, all of the process fluid passed to the separation-disproportionation reaction section of the process passes through at least one disproportionation reaction zone for contact with the ion exchange resin therein.

20 Upon leaving reaction zone 90, the reaction mixture of silicon tetrachloride and chlorosilanes is recycled by 56 to initial distillation zone 60. The mixture of silane and chlorosilanes leaving reaction zone 100 are passed through line 54 to third distillation zone or column 80 having reboiler 82 and reflux condenser 81 to form a product silane overhead stream and a chlorosilane-rich bottom stream, which is recycled in line 55 to said second column 70. High purity silane product is recovered from column 80 through line 51. The operation of column 80 can be controlled so that silane in the overhead stream is separated from diborane which is removed in the bottom stream. In addition to ensuring that all of the process fluid passes through at least one disproportionation reaction

zone, the invention eliminates one distillation-reactor pair from the Fig. 1 arrangement, providing a desirable decrease in processing complexity and equipment costs.

10 The process embodiment of Fig. 2 is a generally preferred embodiment in which the first separation column is used to accomplish recycle of silicon tetrachloride, the third column is used to separate overhead silane product which can be of ultrahigh purity, and the intermediate second column is used to separate fractions each of which passes to a disproportionation reaction zone. While the third column can be employed to assure separation of ultrahigh purity silane from the closest higher boiling boron impurity, i.e. diborane, the process of the invention accomplishes, in a simplified and desirable manner, a process flow ensuring that all of the process fluid passes through at least one disproportionation reaction zone so that the ion exchange resin therein can effectively entrap and remove boron impurities therefrom. Operation of the third column so as to ensure separation of diborane from
20 product silane thus becomes a desirable redundancy imperative to ensure the production of ultrapure silane on a continuing basis in practical commercial operations.

It will be understood that various processing changes can be made within the scope of the invention. Thus, the third column 80 can be replaced by a condenser zone or unit from which liquid dichlorosilane and mono-chlorosilane condensed therein can be recycled to the intermediate column 70 is in the drawing. The high purity silane recovered from said condenser unit will generally have a purity of about 97-99% and may contain from about 1-3% .

monochlorosilane. Such chlorine material is the only significant impurity normally present in said product silane, which is essentially free of electronically active impurities, such as boron, to ultrahigh purity levels as a result of passage through the disproportionation stage as indicated above. The high purity silane may be purified by passage through an additional purification zone to remove monochlorosilane from the silane product gas stream. The purification zone can be in the form of carbon traps comprising beds of activated carbon, silica gel or other commercially available adsorbents. The adsorbent can be regenerated by the usual thermal rising process arrangement. Alternately, said purification zone may comprise a cryogenic or very low temperature distillation zone in which the high purity silane is distilled under reduced pressure, with purified silane being removed as an overhead product. Trace quantities of monochlorosilane and residual impurities that may not have been removed by the ion exchange resin in said disproportionation reaction zones are separated from said purified silane in the cryogenic distillation zone. The cryogenic zone would be operated to ensure that said diborane, B_2H_6 , the lowest boiling electronically active impurity is separated from the silane product. This again provides the highly desirable redundancy that is imperative when ultrahigh purity silane is being produced in practical commercial operation.

It is generally known by those skilled in the distillation art that either gas or liquid overhead or bottom draws can be produced by appropriate adjustment of the reboiler/reflux condenser heat duty. While it is preferred that the liquid phase be utilized for all process streams between the columns and the disproportionation reac-

tion zones, it is within the scope of the invention for some said streams to be in the vapor phase. Both the distillation columns and the disproportionation reaction zones can be operated successfully with either the liquid or the vapor phase.

The process as illustrated in Fig. 2 can be operated at essentially constant pressure operation apart from the normal pressure drop for fluid movement from one zone or column to another and across said zones or columns. It is also within the scope of the invention to allow for

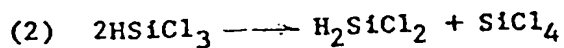
different pressure operation in each of the distillation columns. This can be accomplished by incorporation of appropriate pumps and valves to either boost the pressure, as desired, or to let down pressure on any transfer streams. The preferred pressure for the three columns is different, with the first column 60 keyed to trichlorosilane as the overhead. This column is preferably operated at about 50 psia, with the desirable range extending as low as 30 and as high as 80 psia. Second column 70, which is keyed to dichlorosilane as overhead, is preferably operated at about 300 psia, with the desirable range being from about 250 to about 350 psia. Third column 80, keyed to the ultrahigh purity silane product, is preferably operated at about 350 psia, with a desirable range of from about 300 to about 400 psia. It is also within the scope of the invention to operate column 80 and reactor zone 100 at pressures as low as about 2 psia, thereby enhancing the separation between silane and diborane. Each column can be driven by appropriate heat addition of the reboiler and heat extraction in the reflux condenser corresponding to the temperatures that correspond to said pressure limits. Normally, the use of low pressure steam for the reboilers will be satisfactory along with cooling water for the reflux condenser, although the final silane column may require the use of lower boiling refrigerant as for the cryogenic separation of ultrahigh purity silane from diborane.

It should also be noted that the temperature and pressure employed in the disproportionation reaction zones are not limited to conditions dependent on the conditions in the intermediate column that supplies feedstocks to said zones. Appropriate pumps and valves can be combined with desired cooling or heating steps to assure that the pressure and temperature conditions for said reaction zones can be

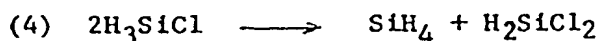
adjusted for optimum operation in accordance with established practice.

As indicated above and as known in the art, the disproportionation reaction zones will contain suitable commercially available ion exchange resin capable of catalyzing the disproportionation reaction. Such resin is commonly insoluble, solid anion exchange resin containing tertiary amino or quaternary ammonium groups bonded to carbon, with such resins that are macroreticular and that contain tertiary amino groups being generally preferred. Such resins, including the commercial macroreticular tertiary amine ion exchange resin produced by Rohm and Haas Company and sold under its Amberlyst A-21 trademark are described in detail in the Bakay patent, U.S. 3,968,199, which also describes the generally known features of the disproportionation reactions. It should be noted that it is generally convenient to employ said resin in an amount generally on the order of about 20 lbs. of resin per lb./hr. of product silane produced in the disproportionation zone. It should also be noted that the disproportionation reactors can be operated in either vapor or liquid phase.

Disproportionation reaction zone 90 is operated in the presence of such ion exchange resin at a temperature capable of causing the disproportionation of trichlorosilane according to reaction (2) as follows:



Disproportionation reaction zone 100 is similarly operated so as to dissociate dichlorosilane according to reactions (3) and (4) below:



10 The capability of the ion exchange resin employed in the disproportionation reaction zones to remove boron impurities is, of itself, known in the art. The process of the present invention, however, ensures that all of the process fluid, i.e. the tri- and dichlorosilane from the hydrogenation step of the integrated process, passes through at least one reaction zone containing such resin so that a very high degree of boron removal occurs to achieve less than 1 ppb impurity levels. Such low levels are acceptable for the desired ultrahigh purity silane used in the production of ultrahigh purity silicon for enhanced solar cell and for electronic applications.

20 The final distillation column of the preferred embodiment illustrated herein can serve to reduce the boron impurity level to any desirable extent since, as long as the impurity is heavier than the desired product, i.e. has a lower relative volatility than the product, the incorporation of additional stages in the final distillation column 80 will serve to reduce the impurity level of the product as desired. This boron removal ability, combined with the assurance provided by the present invention that effective boron removal from the entire process fluid passing through the separation - disproportionation portion of the process, not only ensures desirable redundancy for continuous processing operations but enables boron levels well below one-half part per billion. The silane purity obtained in practical commercial operations of the invention can thus

be of exceptional quality for further processing in solar cell and electronic applications.

The overall integrated process of the invention, in its preferred embodiments, advantageously includes the enhanced initial production of trichlorosilane from metallurgical grade silicon. Apart from the inherent advantages of the reaction of metallurgical silicon, hydrogen and silicon tetrachloride, the reaction can be carried out at elevated pressure and temperature levels that substantially enhance the production rate obtainable in the hydrogenation reaction zone. The reaction zone is maintained at a temperature of from about 400°C to about 600°C, preferably at from about 500°C to about 550°C. The reaction zone, which may comprise a fluid bed, fixed bed or stirred bed, is maintained at pressures in excess of 100 psi, e.g. from about 300 psi to about 600 psi, preferably from about 400 psi to about 600 psi, although even greater yields may be obtained at pressures above 600 psi. Under such conditions, it has been found that the yield of trichlorosilane is significantly improved, said yield being on the order of 15-20 mole% at atmospheric reaction conditions, about 20-25% at 60 psi and over 30% at pressures greater than 100 psi. Larger quantities of the desired trichlorosilane are thus obtainable from smaller size reactors, this feature contributing significantly to the production of low-cost silane and silicon as compared with conventional processing.

The production of trichlorosilane by the reaction of metallurgical silicon with HCl at about 300°C, by comparison, requires relatively large reaction vessels and produces a reaction product mixture containing appreciable quantities

of polysilane, which results in additional processing costs not encountered in the practice of the present invention.

While not essential, it is desirable to employ a copper catalyst in the hydrogenation reactor zone. For this purpose, metallic copper or a mixture of said metallic copper and copper oxides, such as obtained by conventional copper precipitation processing, can be employed. Metallic copper will generally be employed at about 150 mesh, similar to ground up silicon, with said copper oxides being of fine range, such as about 10 microns in size. Cu Cl_2 is also operable for such purposes. The copper catalyst is employed in an amount within the range of from about 0.1% to about 5% by weight based on the overall weight of metallurgical silicon and said copper catalyst employed in the reaction zone.

The hydrogenation reaction zone constitutes a relatively small first stage of the overall process, utilizing an energy efficient sized reactor having decreased utility costs as compared with those that would be required at lower, more conventional, reaction pressure levels. It should be noted that, although relatively high reaction pressures are employed, such pressures do not require the additional level of construction techniques, complexity and costs encountered in the construction of reaction vessels for operation at pressures greater than 600 psi. The simplified waste

disposal operations of the invention are accomplished by condensing a minor portion of the unreacted silicon tetrachloride in the trichlorosilane gas stream removed from the reaction zone prior to its passage to the distillation zone in which silicon tetrachloride is separated from di- and trichlorosilane for recycle to the hydrogenation reaction zone. As such recycle is an important aspect of the overall processing advantages inherent in the integrated and improved process, it will be understood by those skilled in the art that the temperatures and pressures are adjusted so that as little silicon tetrachloride as possible is condensed to achieve the desired impurity removal, thereby maximizing the silicon tetrachloride available for recycle. By this convenient means, carryover metallurgical silicon powder, metal halides and other impurities present in the trichlorosilane gas stream from the hydrogenation reaction zone separate therefrom with said condensed silicon tetrachloride. Such impurities include metal halides, and small amounts of copper if such copper catalyst is employed. Because of the absence of appreciable quantities of the more hazardous polysilanes encountered in conventional processing, said unreacted silicon tetrachloride and accompanying silicon powder and impurities can be passed to waste without the necessity of diluting the waste stream with additional silicon tetrachloride prior to hydrolysis thereof during waste disposal.

In the embodiments of the integrated process in which silicon is to be produced, the silane obtained as disclosed above is passed to a silane decomposition zone, represented generally by the numeral 101 in the drawing, in which the silane is decomposed to form high purity or ultrahigh purity polycrystalline silicon and by-product hydrogen according to the following reaction:



10 The silicon thus obtained can readily be separated from by-product hydrogen and recovered for further refinement or use. In one embodiment, said high purity polycrystalline silicon can be passed, preferably directly, to a melting zone maintained at a temperature above the melting point of silicon, thereby obtaining a high purity, polycrystalline silicon melt from which high purity single crystal silicon can be obtained by known crystal pulling techniques for use in solar cell or electronic applications.

20 It is desirable to decompose silane on a continuous or semicontinuous basis at relatively high production rates, overcoming the inherent disadvantages and limitations of the Siemens process, utilizing either a free space reactor or a fluidized bed reactor. In the free space reactor approach, high purity polycrystalline powder is conveniently produced by introducing silane into the hot free space of a decomposition zone maintained at a temperature within the decomposition temperature range of the silane and below the melting point temperature of silicon, i.e. from about 390°C to about 1400°C, preferably from about 800°C to about 1000°C. As a result of the homogeneous decomposition of the silane within the free

space reactor, polycrystalline silicon powder is formed together with by-product hydrogen. The decomposition can be carried out at essentially atmospheric conditions or at elevated pressures up to 100 psi or above, with elevated pressures tending to form higher silicon production rates and the formation of larger particles, which generally range from submicron to low micron size, e.g. 5 μ . The silane feed gas is preferably introduced into the free space zone turbulently, as by injector means positioned at the top of the reactor, with the turbulence tending to minimize heterogeneous decomposition at the reactor wall and consequent silicon wall deposit build-up. The silicon powder of high purity, upon discharge from the decomposition reactor, may be consolidated or melted for further processing by conventional means to produce a low-cost, high purity single crystal material. In passing the silicon powder from the settling zone in which it is separated from by-product hydrogen, typically within the reactor itself, the silicon powder can advantageously be passed directly to a melting zone, without outside contact, so as to minimize exposure of the product polycrystalline silicon to sources of potential impurities, thereby assuring the high quality of the product silicon. Alternately, the silicon powder may be passed to a consolidation zone to form larger sized silicon particles for subsequent treatment or use.

In another embodiment of the integrated process, the silane decomposition zone comprises a fluid bed silicon reaction zone. In this embodiment, silane is injected into the reaction chamber containing particles of elemental silicon small enough to be fluidized by the injected silane

gas. The fluidized bed of silicon particles are maintained at a temperature within the thermal decomposition range and below the melting point of silicon. By the heterogeneous decomposition of the silane, the desired silicon product is deposited on the fluidized bed particles, which increase in size until removed from the reaction chamber as product. Seed particles for the fluidized bed are formed by the grinding of a portion of the product silicon particles in a manner avoiding the introduction of impurities into said seed particles.

The by-product hydrogen formed upon decomposition of silane in the free space reactor or in a fluid bed reactor can be effectively utilized in the integrated process of the invention. For example, the silane feed to the decomposition zone is advantageously diluted with at least a portion of said by-product hydrogen prior to being introduced into said zone. Likewise, said by-product hydrogen, or at least a portion thereof, can be effectively utilized by being passed to the hydrogenation reaction zone for reaction therein with metallurgical grade silicon and silicon tetrachloride in the initial step of forming the trichlorosilane gas stream from which silane is produced as herein described.

The process of the invention can be employed in the production of silane in accordance with the embodiment illustrated in the drawing, with metallurgical grade silicon, hydrogen and silicon tetrachloride being reacted with said silicon and hydrogen being employed in approximately a 1:2 mole ratio. The hydrogen and silicon tetrachloride, employed in a 1:1 mole ratio, can be preheated to

500°C and pressurized to 325 psig prior to being introduced into the hydrogenation reactor. The trichlorosilane gas stream leaving the reactor is desirably at 500°C and 300 psig. A condenser unit is employed to condense a portion of the silicon tetrachloride content, i.e. about 5%, said silicon tetrachloride carryover silicon powder and impurities being withdrawn from the system through a settler zone, the waste stream being discharged from the system. One portion of the condenser unit is operated 25°C for this purpose, the other portion thereof being operated at about -15°C with hydrogen thus being recycled at -15°C. The trichlorosilane stream is fed to distillation column 60 at 50 psig., with recycle silicon tetrachloride exiting from said column at 124°C and 50 psig. The di- and trichlorosilane stream removed from column 60 is passed through line 53 to column 70, operated at 310 psia, from which a dichlorosilane-rich overhead stream is removed through line 58 and a trichlorosilane-rich bottom stream is removed through line 57. Each stream is passed to a disproportionation zone, assuring that all of the process fluid passing through the separation-disproportionation portion of the process passes through at least one such zone for contact with ion exchange resin therein. The overhead stream is passed to reaction zone 100, from which the resulting disproportionation reaction mixtures is passed to third column 80 operated at 350 psia. The overhead therefrom is product silane, said column being operated to further ensure that the lowest boiling electronically active impurity, diborane, is separated from product silane. The bottom stream from said column 80 is recycled to intermediate column 70

through line 55.

In the practice of the alternate embodiment in which the third distillation zone is replaced by a condenser unit, the condenser is conveniently operated, in the first stage thereof at -30°C and in the second-at -60°C so as to separate and recover product silane and to return all other material to the system. High purity silane recovered from the condenser unit, is at -40°C and 40 psig, is passed to purification zone 101 in which carbon traps are employed to remove trace amounts of monochlorosilane from the silane product.

The effectiveness of vapor phase boron removal from chlorosilanes, as well as the desirable removal of phosphorous impurities that may be present in the chlorosilane-containing process fluid treated in accordance with the invention, was demonstrated in a laboratory test employing the Amberlyst A-21 ion exchange resin referred to above. In this test, a five-gallon container of 99.9% pure trichlorosilane was doped with BCl_3 and PCl_3 to levels 10,000 times higher than usually encountered. Thus, the trichlorosilane feed material was initially found to contain 5 parts-per-million on a wt. to wt. basis (ppm) boron and 75 ppm phosphorous and, upon re-sampling, was analyzed as containing 11 ppm boron and 40 ppm phosphorous. Simple distilling of this feed material to produce an appropriate vapor feed, with recondensing with a 0°C cold finger into quartz flasks resulted in control levels of 2 ppm boron and 12 ppm phosphorous. This distillation corresponds to the passage of the chlorosilane-containing

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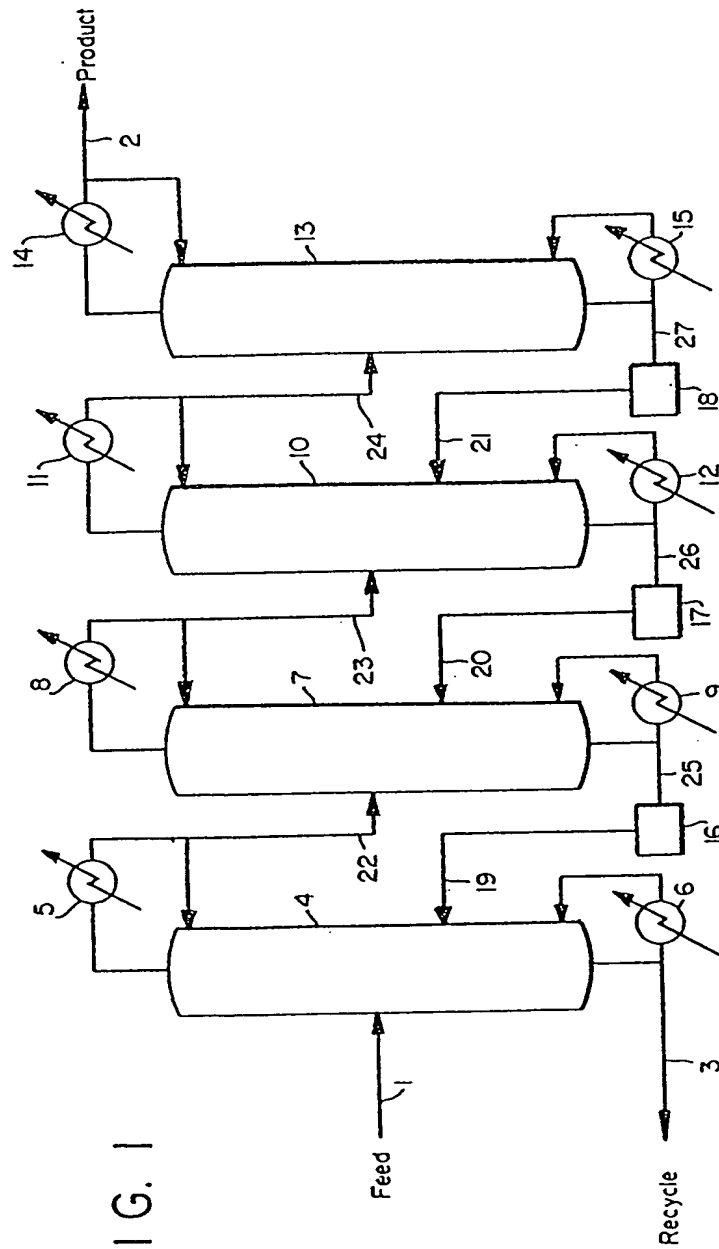
process fluid to initial column 60 in the process flow illustrated in Fig. 2. The vapor feed was passed at 35°C through said Amberlyst A-21 resin, reducing the boron impurity content of the feed gas by a factor of 1,000. Thus, the boron content of the treated gas was 4.3 parts-per-billion (ppb), with said resin also serving to lower the phosphorous content to 125 ppb, i.e. by a factor of 100. The practice of the present invention ensures that all of the process fluid containing di- and trichlorosilane, typically with a boron impurity content of about 10-50 ppb, passing to the separation-disproportionation zone actually contacts ion exchange resin therein to ensure effective reduction in boron impurity levels as is desired for low-cost, ultrahigh purity silicon applications. The Amberlyst A-21 resin has the added desirable feature of concurrently achieving an effective removal of phosphorous from the trichlorosilane vapor stream.

The production of high purity silane and silicon, particularly with very low impurity levels consistent with the production of ultrahigh purity material, is enhanced by the novel separation-disproportionation process of the invention and its incorporation in the overall integrated process for producing silane and silicon by the hydrogenation of metallurgical grade silicon. By ensuring that all of the process fluid passing through the separation-disproportionation zone, apart from the unreacted silicon tetrachloride recycled from the first distillation column 60, passes through at least one disproportionation reaction zone having suitable ion exchange resin therein, the invention contributes significantly to the effective removal of boron

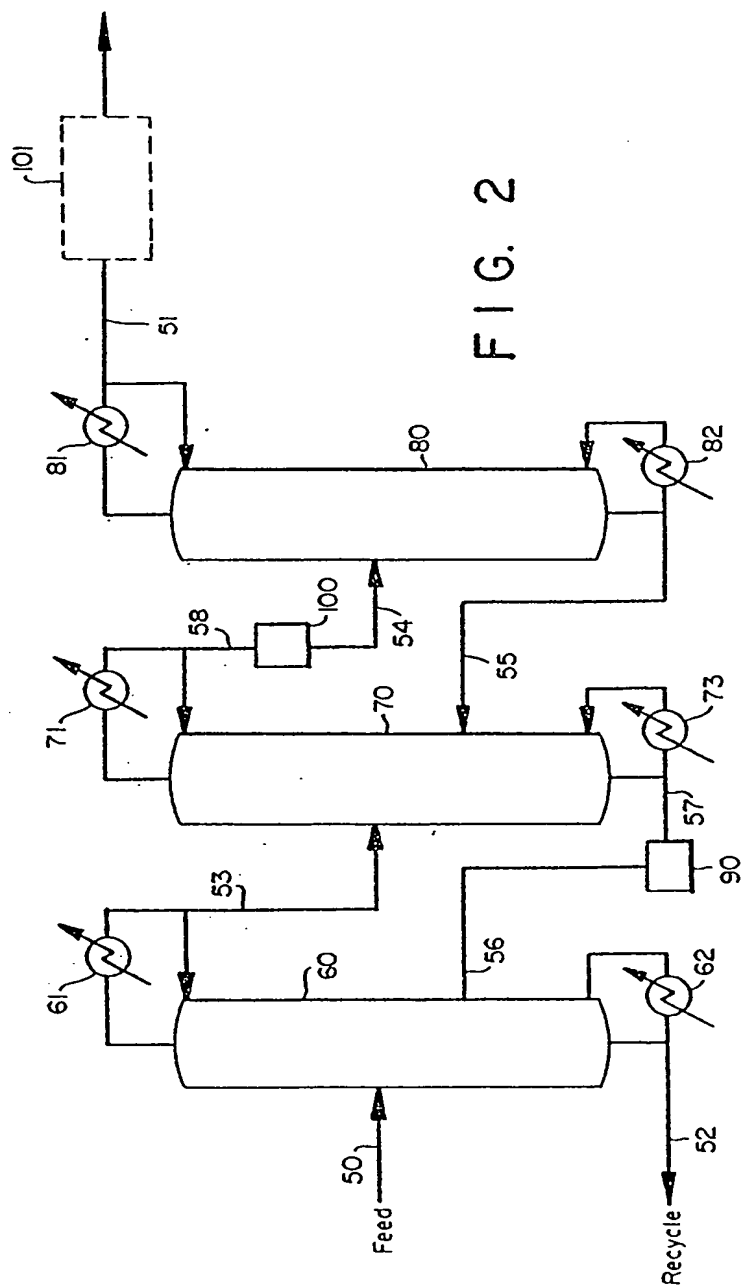
impurities to the very low levels required for the production of ultrahigh purity material. The particular processing arrangement of the invention, in which the overhead gas stream and the bottom stream from intermediate column 70 both pass to disproportionation reaction zones not only ensures effective removal of boron impurities to desirably low levels, but provides for a desirable reduction in necessary equipment requirements and in processing complexity, contributing to the highly advantageous lowering of the cost of high purity silane and silicon achieved by the use of the overall integrated process as described herein. The invention thus represents a very significant improvement in the silicon art, enhancing the prospects for the development of silicon for low-cost, commercially feasible solar cell and electronic applications.

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W. G. Popple



W. G. Hopy



WHAT IS CLAIMED IS:

1. In the process for the production of silane from metallurgical grade silicon in which said silicon is reacted with hydrogen and silicon tetrachloride at elevated temperature and pressure to form trichlorosilane and dichlorosilane, said tri- and dichlorosilane are separated as overhead from unreacted silicon tetrachloride in a first distillation zone, and in which said tri- and dichlorosilane are subjected to a temperature causing disproportionation thereof in the presence of a solid anion exchange resin to form product silane that is separated from by-product mono-, di-, and trichlorosilane and silicon tetrachloride that are recycled, the improvement comprising:

(a) separating said overhead stream in a second distillation zone to form a dichlorosilane-rich overhead stream and a trichlorosilane-rich bottom stream;

(b) subjecting said dichlorosilane-rich stream to temperature and pressure conditions capable of causing the disproportionation thereof in a first disproportionation reaction zone containing an ion exchange resin capable of catalyzing said disproportionation reaction, thereby forming a mixture of silane and chlorosilanes;

(c) subjecting said trichlorosilane-rich stream to temperature and pressure conditions capable of causing the disproportionation thereof in a second disproportionation reaction zone containing an ion exchange resin capable of catalyzing said disproportionation reaction, thereby forming a mixture of chlorosilanes and

silicon tetrachloride;

(d) recycling said mixture of chlorosilanes and silicon tetrachloride to said first distillation zone;

(e) separating said mixture of silane and chlorosilanes in a third distillation zone to form a product silane overhead stream and a chlorosilane-rich bottom stream;

(f) recycling said chlorosilane-rich stream from said third distillation zone to said second distillation zone; and

(g) recovering silane product from said third distillation zone,

whereby it is ensured that all of the process fluid thus treated in said distillation and reaction zones actually passes through at least one said reaction zone for contact with the ion exchange resin therein, said resin serving to remove boron impurities that may be present in said fluid and thereby ensuring a desirably low level of boron impurities in the silane and enabling the production of an ultrahigh purity silane product.

2. The process of claim 1 in which said solid anion exchange resin comprises said resin containing tertiary amino or quaternary ammonium groups bonded to carbon.

3. The process of claim 1 in which first distillation column is operated at a pressure of from about 30 to about ⁸⁰~~70~~ psia, said second column is operated at from about 250 to about 350 psia and said third column is operated at from about 300 to about 400 psia.

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4. The process of claim 3 in which said second column is operated at about 310 psia.

5. The process of claim 3 in which said third column is operated at about 350 psia.

6. The process of claim 3 in which said first column is operated at about 50 psia.

7. The process of claim 1 in which unreacted silicon tetrachloride separated in first distillation zone is recycled for reaction with additional quantities of metallurgical silicon and hydrogen, said metallurgical grade silicon and hydrogen being essentially the only consumed feed materials.

8. The process of claim 1 in which a condenser zone is employed in place of said third distillation zone to form a product silane gas stream and a chlorosilane-rich liquid stream and including treating said silane in a purification zone to remove trace quantities of monochlorosilane therefrom.

9. The process of claim 8 in which said high purity silane is passed through a purification zone comprising a bed of activated carbon.

10. The process of Claim 8 in which said high purity silane is passed through a purification zone comprising a bed of silica gel.

11. The process of claim 8 in which said high purity silane is distilled under pressure in a cryogenic distillation zone, said purified silane being removed as

an overhead product from said cryogenic distillation zone, any trace quantities of monochlorosilane and residual impurities not removed by said ion exchange resin in said first and second reaction zones being separated from said purified silane in said cryogenic distillation zone.

12. The process of claim 2 in which said ion exchange resin is macroreticular and contains tertiary amino groups.

13. The process of claim 7 in which said solid anion exchange resin comprises said resin containing tertiary amino or quaternary ammonium groups bonded to carbon.

14. The process of claim 13 in which said ion exchange resin is macroreticular and contains tertiary amino groups.

15. In the process for the production of polycrystalline silicon from metallurgical grade silicon in which said metallurgical silicon is reacted with hydrogen and silicon tetrachloride at elevated temperature and pressure to form trichlorosilane and dichlorosilane, said tri- and dichlorosilane are separated as overhead from unreacted silicon tetrachloride in a first distillation zone, and in which said tri- and dichlorosilane are subjected to a temperature causing disproportionation thereof in the presence of a solid anion exchange resin to form silane that is separated from by-product mono-, di-, and trichlorosilane and silicon tetrachloride that are recycled, with said silane being decomposed in a

decomposition zone maintained at a temperature within the decomposition temperature range of silane, thereby forming high purity polycrystalline silicon and by-product hydrogen that are readily separated, the improvement composing:

(a) separating said overhead stream in a second distillation zone to form a dichlorosilane-rich overhead stream and a trichlorosilane-rich bottom stream;

(b) subjecting said dichlorosilane-rich stream to temperature and pressure conditions capable of causing the disproportionation thereof in a first disproportionation reaction zone containing an ion exchange resin capable of catalyzing said disproportionation reaction, thereby forming a mixture of silane and chlorosilanes;

(c) subjecting said trichlorosilane-rich stream to temperature and pressure conditions capable of causing the disproportionation thereof in a second disproportionation reaction zone containing an ion exchange resin capable of catalyzing said disproportionation reaction, thereby forming a mixture of chlorosilanes and silicon tetrachloride;

(d) recycling said mixture of chlorosilanes and silicon tetrachloride to said first distillation zone;

(e) separating said mixture of silane and chlorosilanes in a third distillation zone to form a silane overhead stream and a chlorosilane-rich bottom stream;

(f) recycling said chlorosilane-rich stream from said third distillation zone to said second distillation zone; and

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(g) recovering silane from said third distillation zone for passage to said silane decomposition zone, whereby it is ensured that all of the process fluid thus treated in said distillation and reaction zones actually passes through at least one said reaction zone for contact with the ion exchange resin therein, said resin serving to remove boron impurities that may be present in said fluid and thereby ensuring a desirably low level of boron impurities in the silane and in product silicon produced therefrom, thus enabling the production of an ultrahigh purity silicon product.

16. The process of claim 15 in which said solid anion exchange resin comprises said resin containing tertiary amino or quaternary ammonium groups bonded to carbon.

17. The process of claim 15 in which said first distillation column is operated at a pressure of from about 30 to about 70 psia, said second column is operated at from about 250 to about 350 psia and said third column is operated at from about 300 to about 400 psia.

18. The process of claim 17 in which said second column is operated at about 310 psia.

19. The process of claim 17 in which said third column is operated at about 350 psia.

20. The process of claim 17 in which said first column is operated at about 50 psia.

21. The process of claim 15 in which unreacted

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silicon tetrachloride separated in said first distillation zone is recycled for reaction with additional quantities of metallurgical silicon and hydrogen, said metallurgical grade silicon and hydrogen being essentially the only consumed feed materials.

22. The process of claim 15 in which a condenser zone is employed in place of said third distillation zone to form a product silane gas stream and a chlorosilane-rich liquid stream and including treating said silane in a purification zone to remove trace quantities of monochlorosilane therefrom.

23. The process of claim 22 in which said high purity silane is passed through a purification zone comprising a bed of activated carbon.

24. The process of claim 22 in which said high purity silane is passed through a purification zone comprising a bed of silica gel.

25. The process of claim 22 in which said high purity silane is distilled in a cryogenic distillation zone, said purified silane being removed as an overhead product from said cryogenic distillation zone, any trace quantities of monochlorosilane and residual impurities not removed by said ion exchange resin in said first and second reaction zones being separated from said purified silane in said cryogenic distillation zone.

26. The process of claim 15 in which said metallurgical silicon, hydrogen and silicon tetrachloride are reacted at a temperature of from about 500°C to about 550°C at a pressure in excess of 100 psi.

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27. The process of claim 26 in which said pressure is from about 300 to about 600 psi.

28. The process of claim 15 and including condensing a minor portion of said unreacted silicon tetrachloride in the tri- and dichlorosilane stream, carryover metallurgical silicon powder and other impurities present in said stream separating therefrom with the condensed silicon tetrachloride, said impurities thereby being removed from said stream before it passes to said first distillation zone.

29. The process of claim 15 and including passing said high purity silicon separated from by-product hydrogen to a melting zone maintained at a temperature above the melting point of silicon, thereby obtaining a high purity polycrystalline melt from which high purity single crystal silicon can be obtained for solar cell or other applications.

30. The process of claim 15 and including passing at least a portion of said by-product hydrogen to said reaction zone for reaction therein with metallurgical silicon and silicon tetrachloride to form said trichlorosilane.

31. The process of claim 15 in which said silane decomposition zone comprises a fluid bed reaction zone containing a bed of silicon particles upon which silicon is decomposed by the heterogeneous decomposition of silane within said decomposition zone.

32. The process of claim 15 in which said silane

decomposition zone comprises the hot free space zone of a decomposition reactor, said silicon being formed therein as a silicon powder, and including separating said silicon powder from by-product hydrogen.

33. The process of claim 32 and including diluting said silane with at least a portion of said by-product hydrogen prior to being introduced into said silane decomposition zone.

34. The process of claim 32 and including reacting at least a portion of said by-product hydrogen with metallurgical silicon and silicon tetrachloride to form tri- and dichlorosilane.

35. An improved process for the disproportionation of chlorosilanes to produce high purity silane comprising:

(a) separating a process fluid containing tri- and dichlorosilane to a first distillation operation zone to form a dichlorosilane-rich overhead stream from a trichlorosilane-rich bottom stream;

(b) subjecting said dichlorosilane-rich stream to temperature and pressure conditions capable of causing the disproportionation thereof in a first disproportionation reaction zone containing an ion exchange resin capable of catalyzing said disproportionation reaction, thereby forming a mixture of silane and chlorosilanes;

(c) subjecting said trichlorosilane-rich stream to temperature and pressure conditions capable of causing the disproportionation thereof in a second disproportionation reaction zone containing an ion exchange resin capable of catalyzing said disproportionation

reaction, thereby forming a mixture of chlorosilanes and silicon tetrachloride;

(d) separating said mixture of chlorosilanes and silicon tetrachloride in a second distillation separation zone to form a chlorosilane-rich overhead stream and a silicon tetrachloride bottom stream;

(e) recycling said chlorosilane-rich overhead stream to said first distillation zone;

(f) separating said mixture of silane and chlorosilanes in a third distillation separation zone to form a product silane overhead stream and a chlorosilane-rich bottom stream;

(g) recycling said chlorosilane-rich stream from said third operation zone to said first separation zone; and

(h) recovering silane product from said third separation zone, whereby it is ensured that all of the process fluid thus treated in said separation and reaction zones actually passes through at least one of said reaction zones for contact with ion exchange resin therein, said resin serving to remove boron impurities that may be present in said fluid and thereby ensuring a desirably low level of boron impurities in the silane and enabling the production of an ultrahigh purity silane product.

36. The process of claim 35 in which said process fluid contains silicon tetrachloride and including passing said process fluid initially to said second separation zone for separating tri- and dichlorosilanes

from said silicon tetrachloride prior to passing said tri-and dichlorosilane as part of said overhead fed to said first distillation separation zone.

37. The process of claim 36 in which said ion exchange resin comprises a solid anion exchange resin containing tertiary amino or quaternary ammonium groups bonded to carbon.

B 38. The process of claim 36 in which said first distillation ^{column} ~~column~~ is operated at from about 250 to about 350 psia, said second column is operated at from about 30 to about 70 psia, and said third column is operated at from about 300 to about 400 psia.

39. The process of claim 38 in which said first column is operated at about 310 psia.

40. The process of claim 38 in which said second column is operated at about 50 psia.

41. The process of claim 38 in which said third column is operated at about 350 psia.

42. The process of claim 36 in which a condenser zone is employed in place of said third distillation zone to form a product silane gas stream and a chlorosilane-rich liquid stream and including treating said silane in a purification zone to remove trace quantities of monochlorosilane therefrom.

43. The process of claim 37 in which said ion exchange resin is macroreticular and contains tertiary amino groups.

